

Structural and Electrochemical Properties of $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$

Miaomiao Ma, Natasha A. Chernova, Peter Y. Zavalij, M. Stanley Whittingham
Materials Science, State University of New York at Binghamton,
Binghamton, NY, 13902, USA

ABSTRACT

The layered oxide $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$ was synthesized by heating the mixed hydroxide precursor. This 442 composition was found to show high capacity. It has the optimum cobalt concentration to both substantially order the lattice, yet leave enough nickel on the lithium sites to minimize conversion to the 1T structure of CoO_2 on deep charging. A combined x-ray and neutron diffraction study showed conclusively that only nickel, not manganese or cobalt is found on the lithium sites at room temperature. Magnetic measurements also confirmed the presence of nickel on the lithium sites, and showed the effectiveness of cobalt at minimizing nickel disorder. Heating above 800°C always leads to nickel disorder. The structural and thermal stability of reduced lithium content materials was studied; the structure remains rhombohedral except for $x \leq 0.05$, and cobalt substitution improves the thermal stability of the layered compound, but not the chemical stability.

INTRODUCTION

Due to the high cost of LiCoO_2 , cathode materials containing other transition metals have been intensively investigated as an alternative. Among those, LiNiO_2 and LiMnO_2 are the most promising substitutions. However, pure LiNiO_2 without any lithium and nickel cation mixing is hard to synthesis, and LiMnO_2 encounters the phase transition, to spinel, and low cyclability problem. Recently, mixed compounds with all three transition metals, cobalt, nickel, and manganese, synthesized by mixed hydroxide method, have been studied [1-4]. The substitution of cobalt by manganese and nickel lowers the cost and improves the structure stability and capacity. Hence, $\text{LiMn}_y\text{Ni}_z\text{Co}_{1-y-z}\text{O}_2$ has become an attractive cathode material, and many researchers are trying to find the optimum composition with the best performance. Here, we concentrate on the composition $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$, determining its structure, electrochemistry and thermal stability, and comparing it to the compositions $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ and $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$.

EXPERIMENTAL DETAILS

The $\text{LiMn}_y\text{Ni}_y\text{Co}_{1-2y}\text{O}_2$ ($y = 0.33, 0.4, 0.5$) compounds were synthesized by the mixed hydroxide method, followed by high temperature solid-state heating as described in our previous work [3]. Stoichiometric amount of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (99+%, Aldrich), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%, Aldrich), and $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (Aldrich) were dissolved in distilled water and dripped into $\text{LiOH} \cdot \text{H}_2\text{O}$ (98+%, Aldrich) solution with 3 times molar amount of the sum of the metal salts. Precipitates were filtered and washed with distilled water, then heated in an oven at 65°C

overnight. The powder precipitates were then mixed with $\text{LiOH}\cdot\text{H}_2\text{O}$ in molar ratio of $\text{Li}/\text{M}=1.05$ and heated at high temperatures, first at 450°C for 12 hours and then at 800°C for 8 hours.

The electrochemical properties of $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$ as rechargeable lithium battery cathode were examined using coin cells containing pure lithium as the anode at room temperature. The cathode mix contained 80 wt% of $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$ with 10 wt% of PVDF [poly(vinylidene fluoride)], and 10 wt% of acetylene black. The mixture was dissolved in NMP (1-methyl-2-pyrrolidinone), laminated on aluminum foil and vacuum dried at 70°C before use. The electrolyte was 1 M LiPF_6 (lithium hexafluorophosphate) in a 1:1 volume ratio solution of EC (ethylene carbonate) and DMC (dimethyl carbonate) (Merck). 2325 type coin-cells were assembled in a helium glove box. The cells were cycled galvanostatically by connecting to a VMP2 Multi-potentiostat (Princeton Applied Research).

X-ray diffraction data were collected on a Scintag XDS2000 θ - θ powder diffractometer equipped with a Ge(Li) solid state detector and $\text{CuK}\alpha$ sealed tube ($\lambda=1.54178 \text{ \AA}$). Data were measured over the range of 15 - 120° 2θ with a step size of 0.02° step and exposure of 10 sec for structure refinement. Neutron powder diffraction data were collected using the BT-1 32 detector neutron powder diffractometer at the NIST Center for Neutron Research, NBSR. Data were collected over the range of 3 - 168° 2θ with a step size of 0.05° under ambient conditions. The Rietveld refinement was conducted from individual and combined X-ray and neutron powder diffraction patterns using GSAS/EXPGUI package [5].

Scanning electron microscopy (SEM) images were obtained using an Electron Scan instrument at a magnification of 5000. Magnetic measurements were performed using a SQUID magnetometer (Quantum Design MPMS XL-5). The temperature dependences of the magnetic susceptibility ($\chi = M/H$, M is the magnetization and H is the applied magnetic field) were obtained from 298 to 2 K in the magnetic field of 0.1 T. The magnetization curves were measured at 5 K in the magnetic fields up to 5 T.

Chemical delithiation was conducted by mixing 1.2mol/L HF with the active material $\text{LiMn}_y\text{Ni}_y\text{Co}_{1-2y}\text{O}_2$ ($y = 0.33, 0.4, 0.5$) in the ratio of $\text{H}^+/\text{LiMO}_2 = 5:1$. The mixtures were stirred at room temperature for 5 hrs, filtered, washed by acetone, and dried at 100°C .

DISCUSSION

Figure 1 shows the X-ray diffraction pattern of $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$. All the diffraction peaks could be indexed according to the α - NaFeO_2 structure with a space group $\overline{\text{R}}3\text{m}$. The calculated cell parameters a and c were $2.8665(1)\text{\AA}$ and $14.2571(6)\text{\AA}$, respectively. The high values of $c/3a$, 1.58, and the (003)/(104) intensity ratio, 1.75, indicate good ordering of the cations [6]. Rietveld refinement of the X-ray pattern showed a 4.8% of lithium and transition metals mixing. Due to the close scattering of manganese, nickel, and cobalt, x-ray diffraction cannot indicate which metal migrated to the lithium layer. However, manganese, nickel and cobalt have much different neutron scattering factors (Mn -0.373, Co 0.249, Ni 1.03 and Li -0.190). Therefore, a neutron diffraction pattern was used in a combined refinement with X-ray diffraction pattern. It clearly showed that the agreement of X-ray and neutron refinement reached only if the transition metal, which migrates to the lithium layer, has the highest neutron scattering factor, which is nickel. A study of the magnetic behavior as a function of the magnetic field of these layered compounds [4, 7-8] also indicated that some nickel migrates to the lithium particularly for the cobalt free compound $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$.

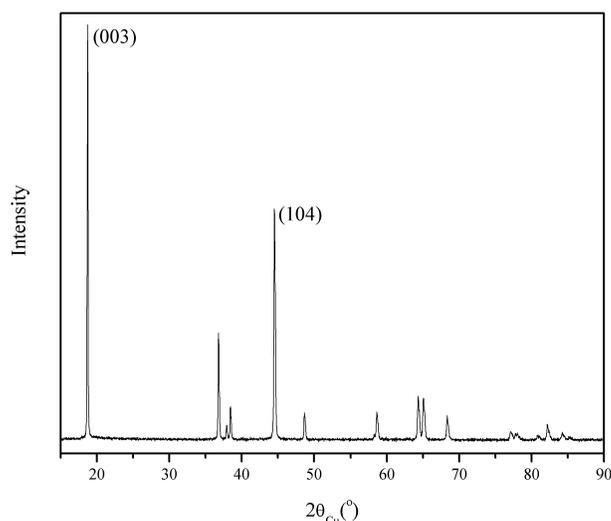


Figure 1. X-ray diffraction patterns of $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$.

Figure 2 shows the cyclic voltammogram of $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$. There is no extra peak around 3V in the cyclic voltammogram indicating that the oxidation state of manganese is not 3+ [6]. There is 0.25V voltage difference between the oxidation peak and redox peak, showing a small polarization during the charge and discharge.

Figure 3 shows the discharge capacity of $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$ between 2.5 and 4.4V at $0.15\text{mA}/\text{cm}^2$ (equivalent to C/10). The initial capacity was $170\text{mAh}/\text{g}$ and most of the capacity fade was observed during the first 20 cycles. Little capacity fade was found between 20 and 40 cycles, and after 40 cycles, the capacity stabilized around $150\text{mAh}/\text{g}$.

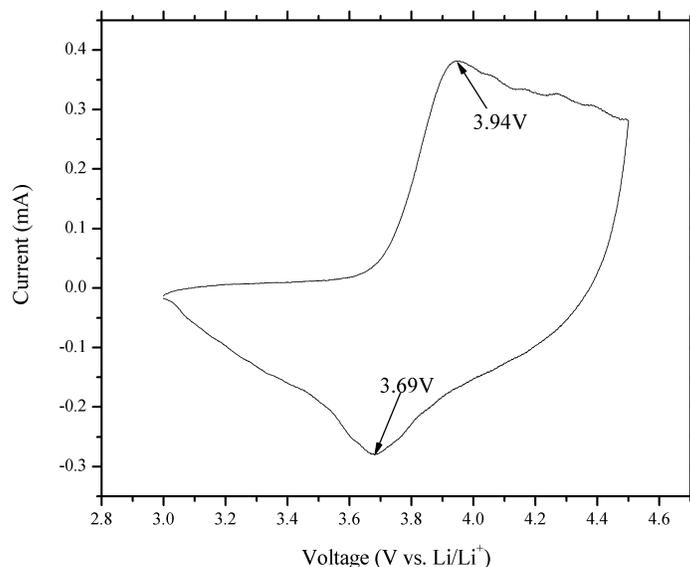


Figure 2. Cyclic Voltammogram of $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$ between 3.0 and 4.5V at $0.1\text{mV}/\text{s}$.

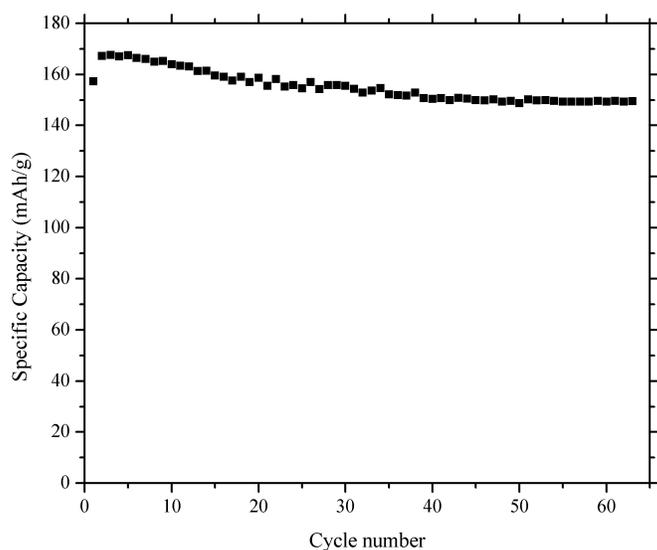


Figure 3. Discharge capacity of $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$ between 2.5 and 4.4V at $0.15\text{mA}/\text{cm}^2$.

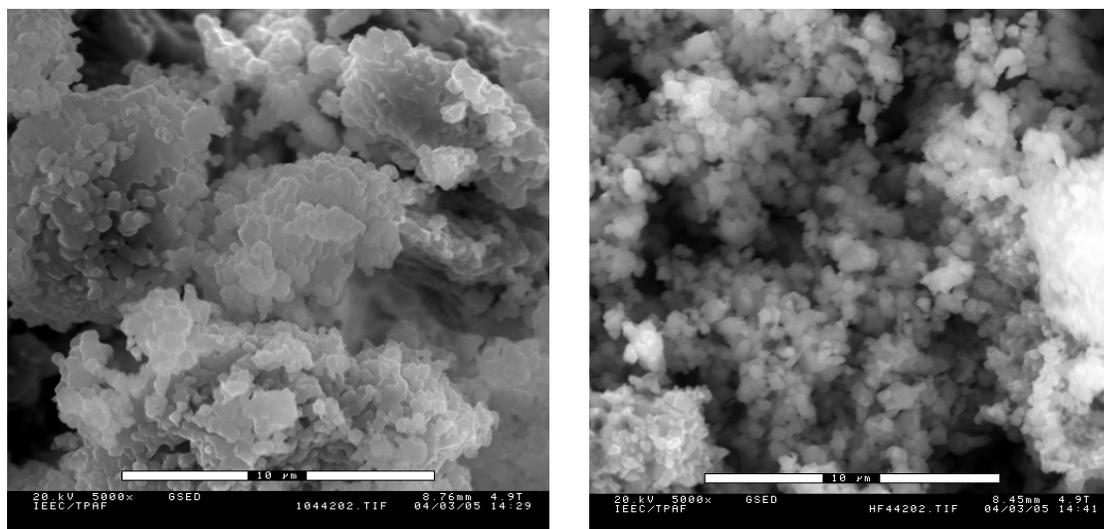
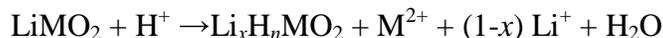


Figure 4. SEM photographs of (left) the initial $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$ and (right) the HF delithiated $\text{Li}_{0.5}\text{H}_n\text{Mn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$ (from [7]).

We earlier studied the electrochemical deintercalation of $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$ in order to monitor any structural changes [4, 7]. That study showed no change in structure until the lithium content, x , dropped to below 0.05 in $\text{Li}_x\text{Mn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$ when a trace of the 1-block 1T structure of CoO_2 was found. The volume change was under 2%, and this combined with the retention of the rhombohedral structure should lead to excellent cyclability; it is the nickel ions in the lithium layer that prevents the structure change by pinning the layers. Thus, it is probably advantageous to intentionally keep some cation disorder [4].

The use of fluoride containing electrolyte salts such as LiPF_6 can lead to the formation of hydrofluoric acid, HF, if any moisture is present in any of the battery components. This can lead

to dissolution of some of the cathode components or to ion-exchange of some of the lithium ions. To determine this effect we made a study of lithium ion-leaching by several acids including hydrofluoric acid from the compounds $\text{LiMn}_y\text{Ni}_y\text{Co}_{1-2y}\text{O}_2$ ($y = 0.33, 0.4, 0.5$). The expected reaction is shown below [9],



The final product from acid leaching contains a small amount of protons. Surface images of the 442 composition before and after leaching are shown in Figure 4. The individual grain sizes were not changed. However, the particles made up by the agglomeration of grains were broken up into their separate grains after acid reaction. The HF treatment caused up to 50% of the lithium to be removed in the case of the 333 composition and less than 10% for the cobalt free compound, suggesting that cobalt causes enhanced reaction. This is consistent with the increased cation ordering observed when cobalt is present; when nickel is present in the lithium layer it will pin the MO_2 layers. Thermal analysis of these reduced lithium content compounds, $\text{Li}_x\text{H}_n\text{Mn}_y\text{Ni}_y\text{Co}_{1-2y}\text{O}_2$ ($y = 0.33, 0.4, 0.5$), indicated that the occurrence of weight loss moved to higher temperatures with increasing cobalt content. Two weight loss steps were observed, the first associated with the protons (that came off as water) and then with oxygen loss associated with nickel reduction and spinel formation.

CONCLUSIONS

Combined Rietveld refinement of X-ray and neutron diffraction patterns showed that the transition metals, Mn, Ni, and Co, are randomly distributed in the 3b layer at room temperature, and only Ni and Li cations were observed in the 3a layer. The magnetic behavior provided further evidence of Ni migration to the Li layers; this migration is reduced with increasing Co content. A small amount of nickel in the lithium layers minimizes formation of the 1T phase on deep charging, thus enhancing the cyclability of the material. Increasing cobalt content enhances lithium leaching by hydrofluoric acid, but stabilizes the lattice against oxygen evolution on heating.

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